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STUDIES OF THE BREAKDOWN MECHANISM OF POLYMERS

VIII. The Thermal Decomposition of a Poly Tetraazolate, Triazole, Oxathiahydrazide, Thiadiazole, and Thiazole

GERHARD F. L. EHLERS

KURT R. FISCH

WILBERT R. POWELL

TECHNICAL REPORT AFML-TR-72-262

MARCH 1973

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. G. F. L. Ehlers (AFML/MBP) as Project Engineer.

This report covers work conducted from March 1970 to April 1971.

The authors wish to thank G. L. Burkett, University of Dayton Research Institute, Dayton, Ohio, for the synthesis of the polythiadiazole used in this study, and L. D. Smithson and the Analytical Branch, Air Force Materials Laboratory, for the high resolution mass spectra of the sublimates and the elemental analyses, respectively.

This report was submitted by the authors in July 1972, has been reviewed, and is approved.



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ABSTRACT

A poly(phenylene)imino tetraazolate, a poly N-phenyl-triazole, a polyoxathiahydrazide, a polythiadiazole, and a polydithiazole were subjected to decomposition in vacuum at temperatures up to 620°C, and the decomposition mechanisms postulated on the basis of the mass spectroscopic data of the volatiles and the mass spectral, infrared, and elemental analysis of condensibles and residues.

A summary of the proposed mechanisms is given in Section IV.

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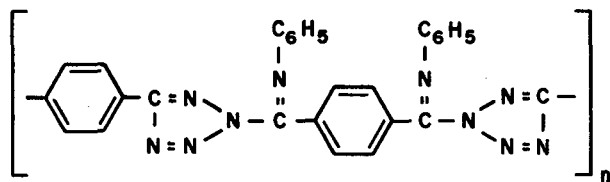
SECTION I

INTRODUCTION

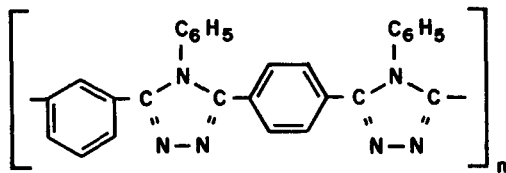
This work is a continuation and conclusion of studies of the thermal breakdown mechanism of aromatic-heterocyclic polymer systems in vacuum. Previous work has been reported in Technical Reports AFML-TR-67-89, 67-295, 67-428, 68-289, 70-63, 71-116, and 72-67.

The following polymers are included in this study:

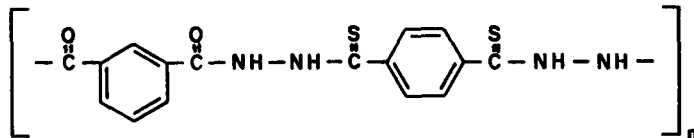
1. Poly(p-phenylene)imino tetraazolate



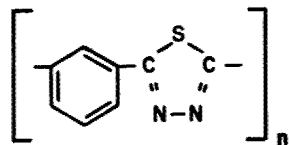
2. Poly(m,p-phenylene)-4-phenyl-1,2,4-triazole



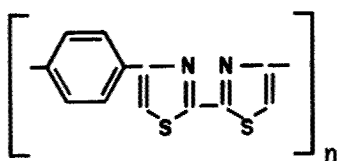
3. Poly(iso/terephthaloyl oxathiahydrazide)



4. Poly(m-phenylene)-1,3,4-thiadiazole



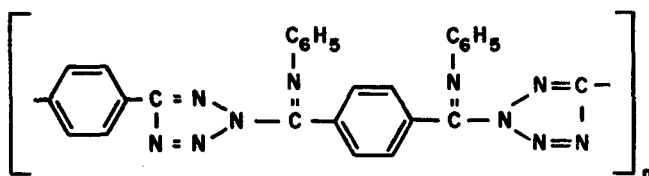
5. Poly(p-phenylene)-dithiazole



The polymers were decomposed stepwise in vacuum in most cases at three different temperatures between 250 and 600°C and the gases analyzed by mass spectroscopy. Residues and sublimates were subjected to elemental analysis, infrared spectroscopy, and high resolution mass spectroscopy.

SECTION II

DISCUSSION

1. Poly(p-phenylene)imino tetraazolate

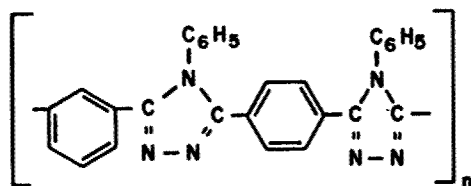
This polymer was prepared by Lilyquist et al. (Reference 1) and was to serve as an intermediate for the preparation of poly(p-phenylene)-4-phenyl-1,2,4-triazole, an approach which was subsequently abandoned. The authors subjected another sample to thermogravimetric analysis and observed a sharp weight loss of 13.3% at 300°C, which compared well with the calculated weight loss of nitrogen during the conversion of the polytetraazolate to the polytriazole.

Elemental analysis of our polymer sample (Table I) indicated that it was neither pure polytetraazolate nor polytriazole and not solely a mixture of the two. The oxygen content of 4.1% suggests the possibility of the presence of some polyoxadiazole. Thermogravimetric analysis (Figure 1) showed a weight loss of about 5% between 260 and 280°C, which seemed to be indicative of the loss of nitrogen. Results of our decomposition studies (Table I) confirm that 86-90% of the volatiles up to 300°C consist of nitrogen. But the results also indicate that the major part of the overall weight loss is made up of condensibles, in other words, larger polymer fragments. With increasing temperatures,

the infrared spectra of the residues (Figure 2) become stronger, and therefore the residues themselves must be more fragmentized; normally, we observe increasingly diffuse bands as a result of crosslinking. As far as a change of absorptions during the decomposition is concerned, the only significant change which can be observed is the appearance of a C=N stretching vibration at 2230 cm^{-1} .

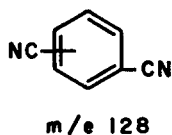
In view of the ill-defined structure of the polymer, a discussion of a possible breakdown mechanism would not be appropriate. It can be noted, however, that the kind and quantities of the volatile products formed are similar to those of the polytriazole discussed next. Such a polytriazole would be expected to be the first product of condensation when heating the polytetraazolate discussed here.

2. Poly(m,p-phenylene)-4-phenyl-1,2,4-triazole

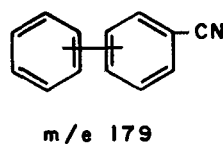
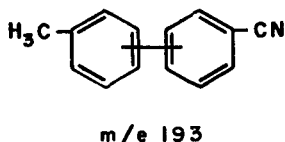
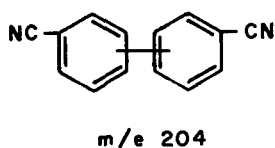


This polymer, as well as the polytetraazolate, was synthesized by Lilyquist et al. (Reference 1). Poly(m,p-phenylene)hydrazide was added to a hot (175°C) solution of excess aniline in polyphosphoric acid. Precipitation with water resulted in a polymer with an elemental analysis fairly close to the calculated amounts (Table II), but probably with some oxadiazole moieties present, as the presence of carbon monoxide and dioxide in the volatile decomposition products suggests. Unfortunately, there was not enough sample available for oxygen analysis, as well as for intermediate

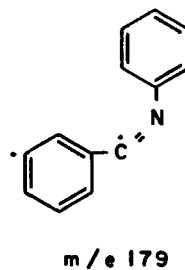
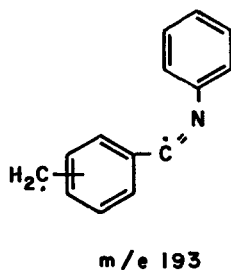
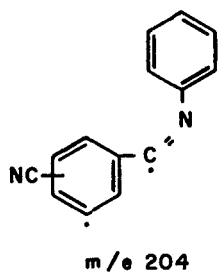
residues and weight loss figures. From TGA (Figure 1), the major weight loss probably occurred in the second temperature step, between 430 and 510°C, the predominant part of this weight loss probably being condensibles. A sample of this condensate was subjected to mass spectroscopy. Peaks as high as m/e 400 were found, with the strongest peak at m/e 128, and other significant peaks at 204, 193, 191, 179, and 161. The major product seems to be phthalic nitrile



(see also the nitrile band at 2200 cm^{-1} in the IR spectrum of Figure 3) and possibly other nitriles, such as



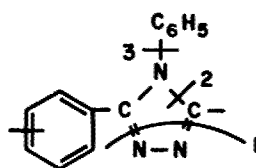
from the rearrangement of radicals such as:



Although benzonitrile has not been found, it may have been present as a liquid film in some parts of the decomposition apparatus.

As far as the volatile products are concerned, the major product appears to be nitrogen, with 1 mole per polymer unit corresponding to the elimination of $=N-N=$ for every second triazole ring. With increasing temperature, more and more hydrogen cyanide is removed, and also more ammonia. It is remarkable that more than just trace amounts of benzene are being formed. The pattern for the remainder of the products is the same as for many of the polymers previously investigated: Absorbed water mainly at the lower temperatures, increasing amounts of methane and hydrogen from the aromatic ring at higher temperatures, and carbon dioxide and carbon monoxide, possibly from some oxadiazole rings. Although total weights of volatiles are not available, it can be assumed that, with increasing temperatures, the amount of carbon dioxide decreases, and that of carbon monoxide increases.

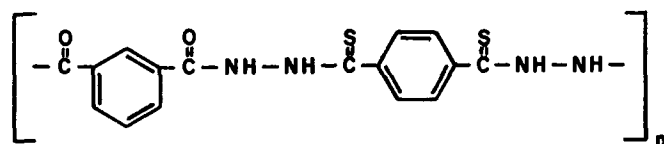
From the above results, the primary decomposition reactions seem to be the cleavage of the triazole ring



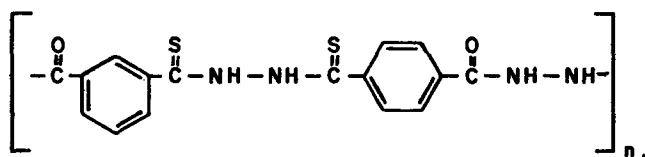
at 1 and 2 to form nitrogen and fragments of the type described above. Some cleavage at 3 accounts for the formation of benzene. With the increasing availability of hydrogen from the decomposition of the aromatic rings, some of the nitrogen is being removed as ammonia, and some of the newly formed nitrile end groups as hydrogen cyanide.

3. Poly(iso/terephthaloyl oxathiahydrazide)

This polymer



has been prepared in 1964 by Frazer et al. from poly(iso/terephthaloyl hydrazide) and P_2S_5 in refluxing pyridine for 30 hours (Reference 2). Although the distribution of the sulfur atoms would be expected to be random, e.g.,



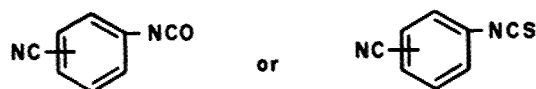
ultraviolet and infrared spectral comparison with authentic ordered and random samples suggested that the structure of this polymer (apparently not identical to ours) was essentially ordered (Reference 3). Films of this polymer can be cast from pyridine or DMAC, and then are supposed to convert to the (insoluble) polythiadiazole by heating at 250-300°C.

Thermogravimetric analysis (Figure 4) of our sample does not reveal a conversion to the polythiadiazole in the indicated temperature range. Analysis of the polymer (Table III) shows a considerable deficiency in its sulfur content, and the following comparison suggests that it may contain a considerable number of oxadiazole units:

	C	H	O	N	S
polyhydrazide	59.3	3.7	19.8	17.3	--
polyoxathiahydrazide	53.9	3.4	9.0	15.7	18.0
polythiadiazole	60.0	2.5	--	17.5	20.0
polyoxadiazole	66.7	2.8	11.1	19.4	--
polymer sample	55.4	3.6	10.5	16.4	9.1

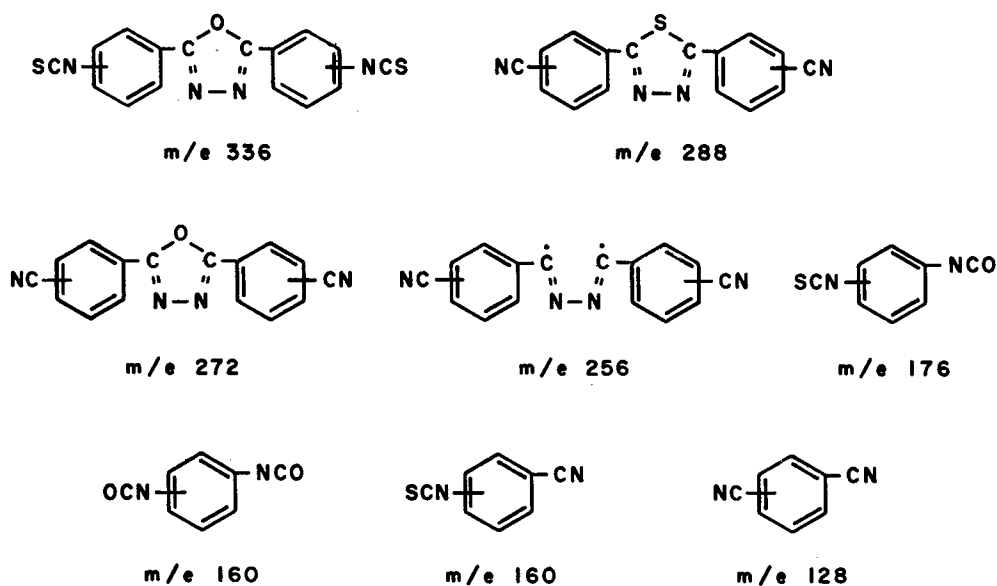
Figures 5 and 6 confirm that the infrared spectra of the polymer and especially of its residue at 280°C have features which are similar to those of the polythiadiazoles as well as the polyoxadiazoles. In addition, the infrared spectrum of the residue displays a nitrile absorption band at 2200 cm^{-1} .

The major product of decomposition was a sublimate, which was investigated in more detail. A small amount of greenish sublimate formed in the cell just above the heating block. This material does not melt below 500°C, and thin-layer chromatography yielded a spot with a diffuse tail. Its IR spectrum, which displays a nitrile band at 2200 cm^{-1} , is shown in Figure 7. The location of its formation suggests a larger polymer fragment with nitrile end groups. A somewhat larger amount of a white-yellowish sublimate formed in the upper part of the decomposition cell. The product melted at 155 to 165°C, and thin-layer chromatography gave a single spot with tetrahydrofuran, and a spot with a diffuse tail with benzene. Its spectrum, with a nitrile band at 2220 cm^{-1} and an isocyanate or thiocyanate peak at 2040 cm^{-1} , can be seen in Figure 7. The melting point suggests the presence of isophthalonitrile (mp 162°C), but the presence of an isocyanate or thiocyanate group points to a structure such as

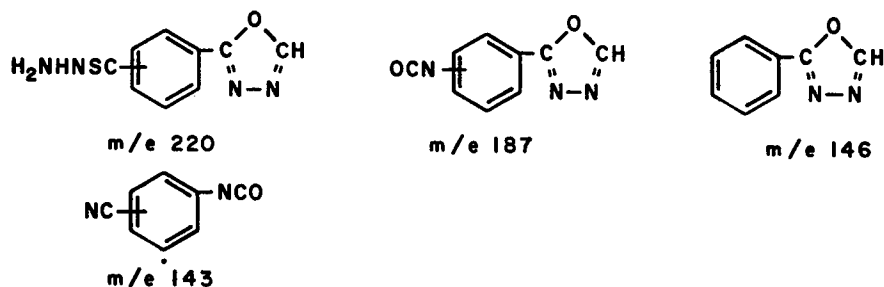


To obtain additional information, a larger amount of sublimate was prepared in a large, evacuated reaction tube. The sublimate could be separated into a white, apparently crystalline, and a yellow product by extraction with hot water; the white material was water soluble. Figure 8

represents the IR spectra of the two materials; both contain the nitrile and the isocyanate/thiocyanate absorptions, but the spectrum of the water insoluble material is more diffuse and may be of higher molecular weight. The mass spectrum of the white compound revealed a molecular ion peak at m/e 288 and a weak one at m/e 334, and the strongest peaks at m/e 128 and 130. Other peaks occurred at m/e 272, 256, 220, 187, 176, 160, 149, 146, 120, 102, 76, 75, and 44. Some possible assignments are:



The mass spectrum of the yellow product has peaks as high as about m/e 500, with the strongest peak at m/e 128 (iso-or terephthalonitrile) and other peaks at 256, 220, 187, 160, 149, 146, 143, 130, 129, 107, 75, 64, and 50. Possible assignments of some of these peaks are:



As far as the volatile products are concerned (Table III), nitrogen is by far the major component; more than 70% of the available nitrogen in the polymer is being removed. Other fragments of oxathiahydrazide, oxadiazole and thiadiazole units, probably present, are carbon dioxide, carbon monoxide, hydrogen cyanide, and hydrogen sulfide. Methane is the major volatile from the decomposition of the benzene rings, while surprisingly little hydrogen is being formed. It can be seen that a good portion of the hydrogen, which may have formed at the higher temperatures, is being used for the formation of hydrogen sulfide and hydrogen cyanide.

It is difficult to propose a mechanism of decomposition in view of the complexity of the original polymer, and the multitude of fragmentation products. In addition, not enough material was available to obtain complete and reliable analysis data of the residues. The major volatile product, nitrogen, most likely resulted from the decomposition of oxadiazole and thiadiazole units, either present in the polymer or formed on heating. The large amount of nitrogen being formed is nevertheless surprising; it involves 72% of the available nitrogen, versus 39% previously obtained for a poly-1,3-phenylene hydrazide (Reference 4), 50% for poly-1,3-phenylene oxadiazole (Reference 4), only 4% for poly-1,4-phenylene oxadiazole (Reference 4) and 1% for the polythiadiazole to be discussed below. From this, one may conclude that meta-substituted oxadiazole (hydrazide) units are the most likely sources of nitrogen.

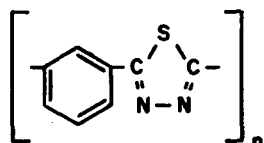
The remainder of the volatile products, and some components of the sublimate, including iso (tere) phthalo nitrile, may have resulted either directly from oxa- or thiahydrazide moieties or from intermediate

oxadiazole or thiadiazole units; a number of the condensation products, however, show that ring formation occurred first (see structures above), or that the rings were already present.

A possible breakdown mechanism for polyhydrazides and polyoxadiazoles has been discussed previously (Reference 4). A proposed mechanism for polythiahydrazides is shown in Figure 9. The decomposition mechanism for 1,3,4-thiadiazoles is discussed below and shown in Figure 12.

4. Poly(m-phenylene)-1,3,4-thiadiazole

The polymer



was prepared according to a procedure by Frazer and coworkers (Reference 2) by refluxing the corresponding polyhydrazide in excess pyridine and P_2S_5 for 120 hours, separating it from the pyridine, washing it repeatedly with hot water and with methanol in a blender and Soxhlet-extracting with methanol.

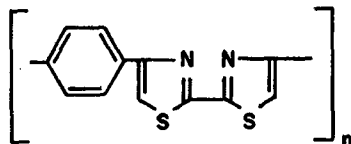
The elemental analysis of the polymer is reasonably close to the calculated values; however, the polymer contains oxygen, probably mostly in the form of oxadiazole units, which accounts for the presence of CO , CO_2 , SO_2 , and OCS in the decomposition products (Table IV). Some water, evolving over the entire temperature range, may result from continued condensation of residual hydrazide units, and traces of methanol from the work-up of the polymer. The major volatile product is H_2S , and

additional sulfur is being removed in the form of CS_2 , SO_2 , $\text{O}=\text{C}=\text{S}$, and some CH_3SH , the latter being obviously the result of the presence of methanol in the polymer. Nitrogen is the second most important volatile, and, along with hydrogen cyanide, accounts for the amount of nitrogen removed from the polymer. Puzzling is the relatively large quantity of hydrogen chloride and the fact, that it is being formed over the entire temperature range. The presence of chlorine is probably the result of $-\text{COCl}$ end groups in the original polyhydrazide. Additional volatiles are benzene, methane, and hydrogen from the aromatic portion of the polymer.

The infrared spectra of the polymer and two of its residues (Figure 10) show as major changes during the decomposition the disappearance of the carbonyl band (1650 cm^{-1}) from residual hydrazide moieties, and the appearance of $\text{C}\equiv\text{N}$ groups between 2200 and 2300 cm^{-1} .

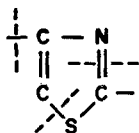
By far the major decomposition product is a yellow sublimate which forms essentially at the 450 to 550°C temperature step (this weight loss coincides with the weight loss step in the TGA curve, Figure 4). The product, which is soluble in acetone, has a melting point of 162°C (DTA, at $20^\circ\text{C}/\text{min}$), and its infrared spectrum is shown in Figure 11. It was identified as isophthalonitrile.

A proposed overall breakdown mechanism for the thiadiazole ring is shown in Figure 12.

5. Poly(p-phenylene)-dithiazole

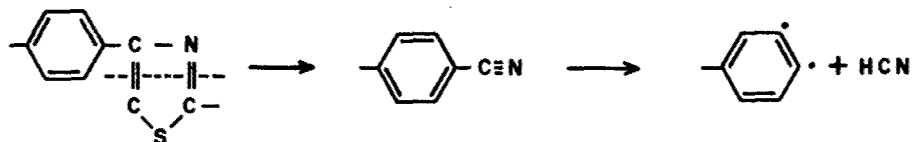
This polymer, which has been obtained from D.T. Longone, University of Michigan (Reference 5), seems to have a number average molecular weight of about 10,000, based on end group analysis, and is highly crystalline, not readily soluble, and non-fusible. Its TGA curve is shown in Figure 4; the gradual weight loss may be caused by different structures and/or a wide molecular weight distribution present in the polymer. Not enough material was available for elemental analysis, but the infrared spectrum (Figure 13) suggests the presence of carbonyl, and the composition of the volatile products confirms that oxygen is present in the polymer (Table V).

At 600°C, the same volatile decomposition products form as in case of the polythiadiazole (Table IV) except for free nitrogen. On the other hand, some CH_3CN is obtained, which may result from a thiazole ring fragment such as



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Also, relatively larger amounts of hydrogen cyanide are formed than in the thiadiazole:



As the weight balance in Table V indicates, a certain amount of condensibles of unknown nature has also been obtained.

SECTION III

EXPERIMENTAL

The apparatus used for the decomposition studies was similar to the one previously described (Reference 6). It consisted of a quartz test cell (the remainder of the apparatus being Pyrex), fitted with a thermocouple well and connected to a sample cell, manometer, vacuum pump, and nitrogen inlet. The test cell was heated by means of an aluminum block, fitted with two 350w heating cartridges and controlled by an F&M Model-240M Power Proportioning Temperature Programmer. The temperature control was within $\pm 3^{\circ}\text{C}$.

The polymer was dried under vacuum at 110°C overnight and 50 to 100 mg was weighed into a quartz crucible. The crucible was placed in the test cell and the system was twice evacuated and flushed with nitrogen. The sample cell was degassed by heating with a heat gun. The system was then evacuated to approximately 5μ and the valves closed. The controller was set at the desired temperature, the furnace was turned on, and temperature, time, and pressure were automatically recorded. When no further pressure increase was noted by means of a photoelectric cell and printout, the accumulated gases were permitted to diffuse into the sample cell. The sample cell was removed, a new cell attached, and the system again evacuated and twice flushed with nitrogen. After reestablishing a vacuum of approximately 5 to 10μ , the furnace temperature was raised to the next higher temperature and the procedure repeated. Test temperature selection for obtaining an appropriate amount of pressure was based on information from TGA and from an exploratory run. The final residue was collected and

subjected to elemental analysis, weight loss determination, and infrared spectroscopy. Residues for the first two temperature steps were obtained by subjecting two separate samples to the identical history of the original sample up to the first two temperatures, respectively. They were also analyzed as indicated above. The sublimate formed was isolated and examined by infrared spectroscopy and high resolution mass spectroscopy.

MASS SPECTROSCOPY OF THE GASES

The gas samples were analyzed in a Consolidated Electrodynamics Corporation Model 21-103B (modified) mass spectrometer. An ionizing voltage of 70 ev and an ionizing current of 10 microamperes was used.

HIGH RESOLUTION MASS SPECTROSCOPY OF THE SUBLIMATES

The sublimes were analyzed in a CEC Model 21-110 mass spectrometer at ionizing voltages of 70 and 15 ev and an accelerating voltage of 8 kv. The samples were introduced via the direct introduction probe at a temperature of 180°C.

INFRARED SPECTROSCOPY

Infrared spectra were obtained by use of a Perkin-Elmer infrared recording spectrophotometer, model 137, and potassium bromide pellets. The polymers and especially the residues were shaken 1 to 4 min. in steel vials in a Wig-L-Bug.

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was performed in a modified Chevenard thermobalance in nitrogen (flow rate 98 cc/min.) at a heating rate of 3°C/min.

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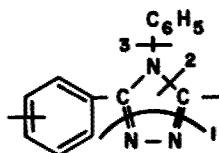
ELEMENTAL ANALYSIS

Elemental analyses were performed by the Analytical Branch, Air Force Materials Laboratory. The data given represent mean values of duplicate runs.

SECTION IV

CONCLUSIONS

A polytetraazolate and its corresponding condensation product, an N-phenyl-substituted polytriazole, on decomposition in vacuum up to 620°C essentially form polymer fragments, frequently with nitrile end groups. The major product is phthalonitrile. Although some benzene was observed, benzonitrile, another likely product, was not found. The most abundant volatile is nitrogen. The products suggest that the following initial cleavages may occur:

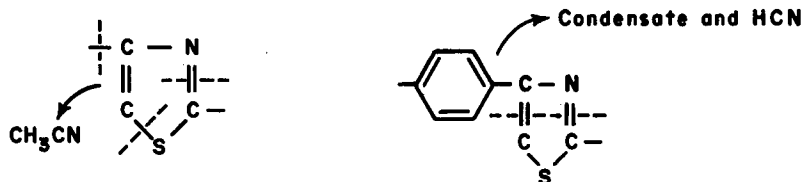


A polyoxathiahydrazide mainly condenses to form oxadiazole and thiadiazole units and H_2O and H_2S , respectively. Both ring systems, in turn, produce polymer fragments, frequently with $-\text{CN}$, $-\text{NCS}$, and $-\text{NCO}$ end groups. Nitrogen is the major volatile product (Figure 9).

Polythiadiazole yields isophthalonitrile as the major solid fragmentation product, in addition to volatiles such as H_2S and N_2 . The proposed breakdown mechanism is shown in Figure 12.

A polydithiazole degrades to form a condensate of unknown structure and essentially the same volatile products as the thiadiazole, but, in

addition, some CH_3CN , and no free nitrogen. Possible cleavage reactions are:



Methane and hydrogen are the usual fragmentation products of the benzene moieties in these polymers.

All polymers contain a certain amount of oxygen, in most cases probably oxadiazole rings, and consequently generate carbon monoxide and carbon dioxide.

Table I
Analysis of Volatiles and Residues of Poly-
(p-phenylene) imino tetraazolate

	C	H	N	O	Resid.
Analysis calc. for $C_{28}H_{18}N_{10}$ (polytetraazolate)	68.0	3.7	28.3	--	
Analysis calc. for $C_{28}H_{18}N_6$ (poly triazole)	76.7	4.1	19.2	--	
Analysis calc. for $C_{16}H_8N_4O_2$ (poly oxadiazole)	66.7	2.8	19.4	11.1	
Found for polymer	72.8	4.3	15.0	4.1	2.5
Found for Residue at 220°C	74.2	4.3	9.2	3.1	2.7
Found for Residue at 300°C	78.0	4.3	11.4	3.8	2.3
Found for Residue at 500°C	82.0	3.8	9.9	3.2	2

Temp. Range °C	Volatile Products (Mole %)											Total		
	C ₆ H ₅ CN	Toluene	Benzene	CO ₂	HCl	CO	N ₂	HCN	H ₂ O	NH ₃	CH ₄	H ₂	Volatiles (Weight%)*	Vol. & Condensibles (Weight %)*
25-200	---	traces	0.1	4.2	0.4	0.9	86.3	0.4	6.2	--	0.7	0.7	1.0	7.9
200-300	---	---	0.1	6.1	---	1.1	90.2	0.2	1.4	--	0.2	0.8	3.2	18.6
300-500	traces	0.6	3.0	20.5	---	12.5	26.4	11.5	4.2	9.0	2.8	9.5	4.7	14.5
Volatile Products (Weight %)*														
25-500	traces	0.1	0.4	1.8	traces	0.6	4.8	0.6	0.2	0.3	0.1	traces	8.9	41.0
Volatile Products (Moles per polymer unit)														
25-500	<0.01	0.05	0.02	0.21	<0.01	0.11	0.85	0.10	0.05	0.07	0.02	0.07		

* of starting material

Table II

Analysis of Volatiles and Residues of

Poly (m, p-phenylene) -4-phenyl-1,2,4-triazole

	C	H	N
Analysis calc. for $C_{28}H_{18}N_6$:	76.7	4.1	19.2
Found for Polymer:	73.8	4.3	15.5
Found for Residue at 620°C:	84.7	2.9	6.3

Temp. Range °C	Volatile Products (Mole %)										Volatiles Vol. & Condensibles (Weight %)*	
	toluene	benzene	CO ₂	N ₂ H ₄	CO	N ₂	HCN	H ₂ O	NH ₃	CH ₄	H ₂	(Weight %)*
25-430	0.2	3.4	8.7	0.7	6.5	73.0	1.5	3.9	1.1	0.5	0.4	
430-510	0.6	5.0	1.6	--	3.7	74.2	6.4	0.3	5.3	0.6	2.3	
510-620	0.3	2.6	1.2	--	5.3	--	11.0	0.6	6.1	9.9	63.0	
* of starting material												
Temp. Range °C	Volatile Products (Weight %)										Volatiles Vol. & Condensibles (Weight %)*	
	toluene	benzene	CO ₂	N ₂ H ₄	CO	N ₂	HCN	H ₂ O	NH ₃	CH ₄	H ₂	(Weight %)*
25-620	0.2	1.7	0.6	0.02	0.8	6.7	1.2	0.1	0.5	0.4	0.3	12.5
25-620	0.01	0.09	0.06	<0.01	0.12	1.05	0.19	0.02	0.13	0.12	0.7	42.6

Table III

Analysis of Volatiles and Residues of

Poly (Iso/terephthaloyl oxathlahydrazide)

	C	H	O	N	S	Ash
Analysis calc. for $C_{16}H_{12}O_2N_4S_2$:	53.9	3.4	9.0	15.7	18.0	--
Found for Polymer:	55.4	3.6	10.5	16.4	9.1	3.5
Found for Residue at 280°C:	60.0	3.0	**	6.0	8.6	
Found for Residue at 400°C:	63.8	2.8	**	6.0	7.9	
Found for Residue at 600°C:	69.8	1.8	**	9.4	5.2	

Temp. Range °C	Volatile Products (Mole %)													Total	
	CHCl ₃	Benzene	CS ₂	SO ₂	CH ₃ SH	CO ₂	H ₂ S	CO	N ₂	HCN	H ₂ O	CH ₄	H ₂	Volatiles (Weight %)*	Vol. & Condensibles (Weight %)*
25-280	1.0	traces	0.6	0.1	0.2	20.3	1.0	2.9	66.7	2.8	4.4	--	--	6.3	19.0
280-400	--	traces	0.9	0.2	0.3	9.5	2.4	4.8	78.3	2.4	0.2	0.7	0.3	8.8	28.0
400-600	--	0.1	1.3	0.2	--	6.7	18.2	20.6	15.4	18.5	0.5	7.0	11.5	7.0	23.7
Volatile Products (Weight %)*															
20-600	0.24	0.02	0.55	0.08	0.06	3.76	1.93	2.06	11.26	1.65	0.19	0.33	0.06	22.1	70.7
Volatile Products (Moles per polymer unit)															
20-600	<0.01	<0.01	0.03	<0.01	<0.01	0.30	0.20	0.26	1.43	0.22	0.04	0.73	0.10		
*) of starting material) not determined															

*) of starting material

**) not determined

Table IV

Analysis of Volatiles and Residues of Poly-

(m-phenylene)-1,3,4-thiadiazole

	C	H	N	S	O	Cl	Ash
Analysis calc. for $C_8H_4N_2S$:	60.0	2.5	17.5	20.0			
Found for Polymer:	58.0	3.0	17.5	18.7	3.1	0.6	0.7
Found for Residue at 300°C:	58.9	2.7	16.6	18.5	2.0	**	
Found for Residue at 450°C:	60.0	2.8	16.5	18.5	1.8	**	
Found for Residue at 550°C:	64.8	1.4	8.1	**	**	**	

Temp Range °C	Volatile Products (Mole-%)															Total	
	Benzene	CS ₂	SO ₂	O=C=S	CH ₃ SH	CO ₂	HCl	H ₂ S	CH ₃ OH	CO	N ₂	HCN	H ₂ O	CH ₄	H ₂	Volatiles (Weight%)*	Vol & Condensibles (Weight %)*
25-300	---	2.1	0.8	0.8	4.7	4.1	15.8	18.7	1.9	4.6	3.1	1.5	37.7	2.6	1.5	0.6	1.7
300-450	---	2.1	traces	3.8	--	5.2	12.5	33.2	--	3.8	30.5	1.2	6.0	0.7	1.0	6.4	10.2
450-550	0.1	3.4	1.1	1.8	--	1.3	13.9	27.7	--	8.7	19.5	10.9	5.4	2.0	4.1	1.7	72.6
Volatile Products (Weight %)*																	
25-550	traces	0.5	0.05	0.5	0.05	0.5	1.3	2.8	0.01	0.4	2.0	0.2	0.04	0.05	0.01	8.8	84.5
Volatile Products (Moles per polymer Unit)																	
25-550	<0.01	0.01	<0.01	0.01	<0.01	0.02	0.06	0.13	<0.01	0.02	0.1	0.01	0.04	<0.01	<0.01		
*) of starting material																	
**) not determined																	

Table V
Analysis of Volatiles of Poly (p-phenylene)-diathiazole

Temp. range °C	Volatile Products (Mole %)														Total	
	toluene	benzene	CS ₂	SO ₂	θ=C-S	CO ₂	CH ₃ CN	HCl	H ₂ S	CO	HCN	H ₂ O	CH ₄	H ₂	Volatiles (Weight%) ^{*)}	Vol & Condensibles (Weight %) ^{*)}
25-600	0.2	0.2	2.2	1.3	1.3	1.2	0.8	7.4	32.2	18.1	20.0	5.0	2.7	7.5	16.6	33.5
Volatile Products (Weight % ^{*)})																
25-600	0.1	0.09	0.9	0.5	0.4	0.3	0.2	1.5	6.1	2.8	3.0	0.5	0.2	0.08	16.6	33.5
Volatile Products (Moles per Polymer Unit)																
25-600	traces	traces	0.03	0.02	0.02	0.02	0.01	0.10	0.43	0.24	0.27	0.07	0.04	0.10		

*) of starting material

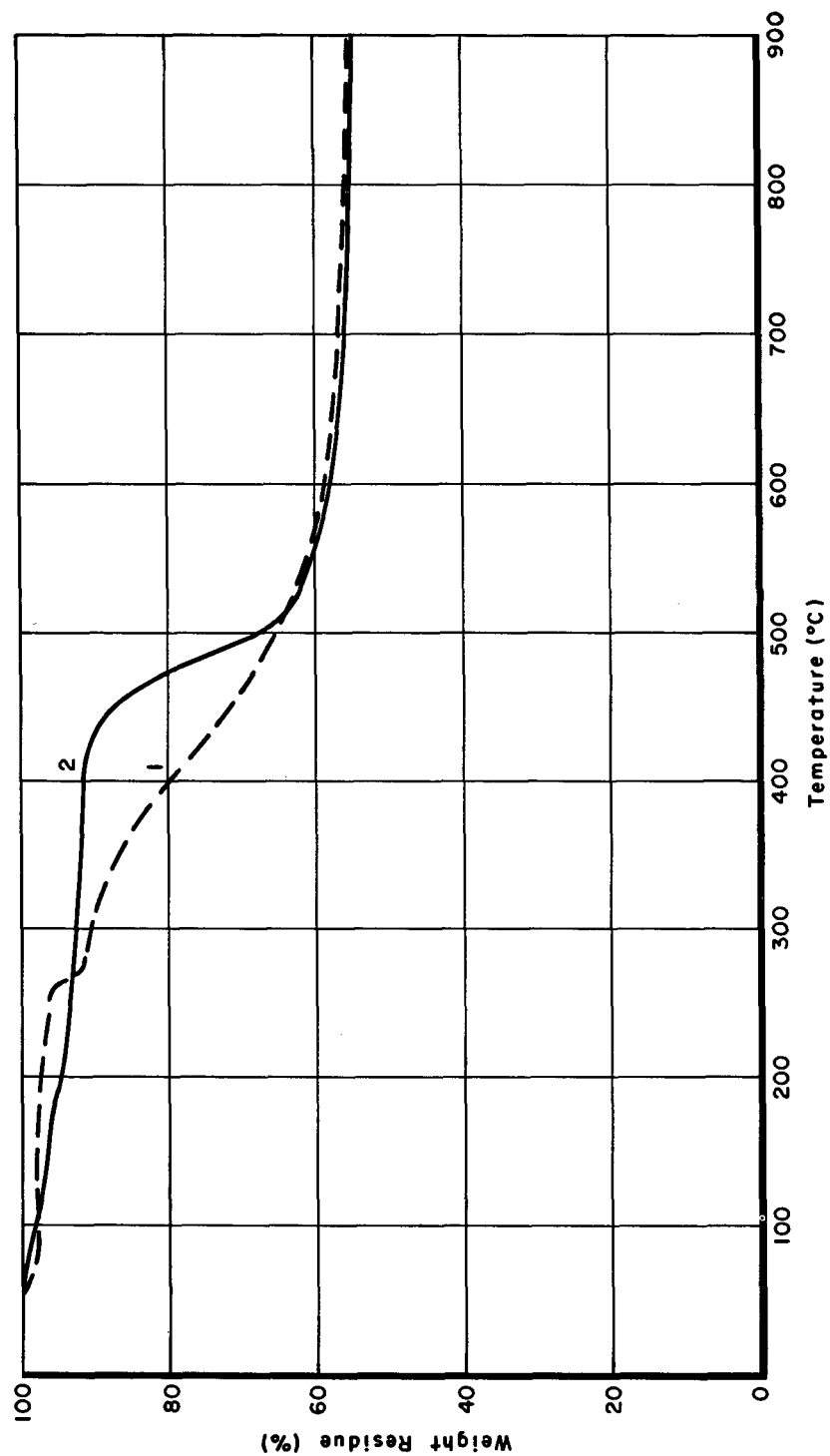


Figure 1. Thermogravimetric Analysis (nitrogen, $\Delta T = 150^\circ\text{C}/\text{hour}$) of 1: Poly(p-phenylene)imino tetraazolate; 2: Poly(m-, p-phenylene)-4-phenyl-1,2,4-triazole

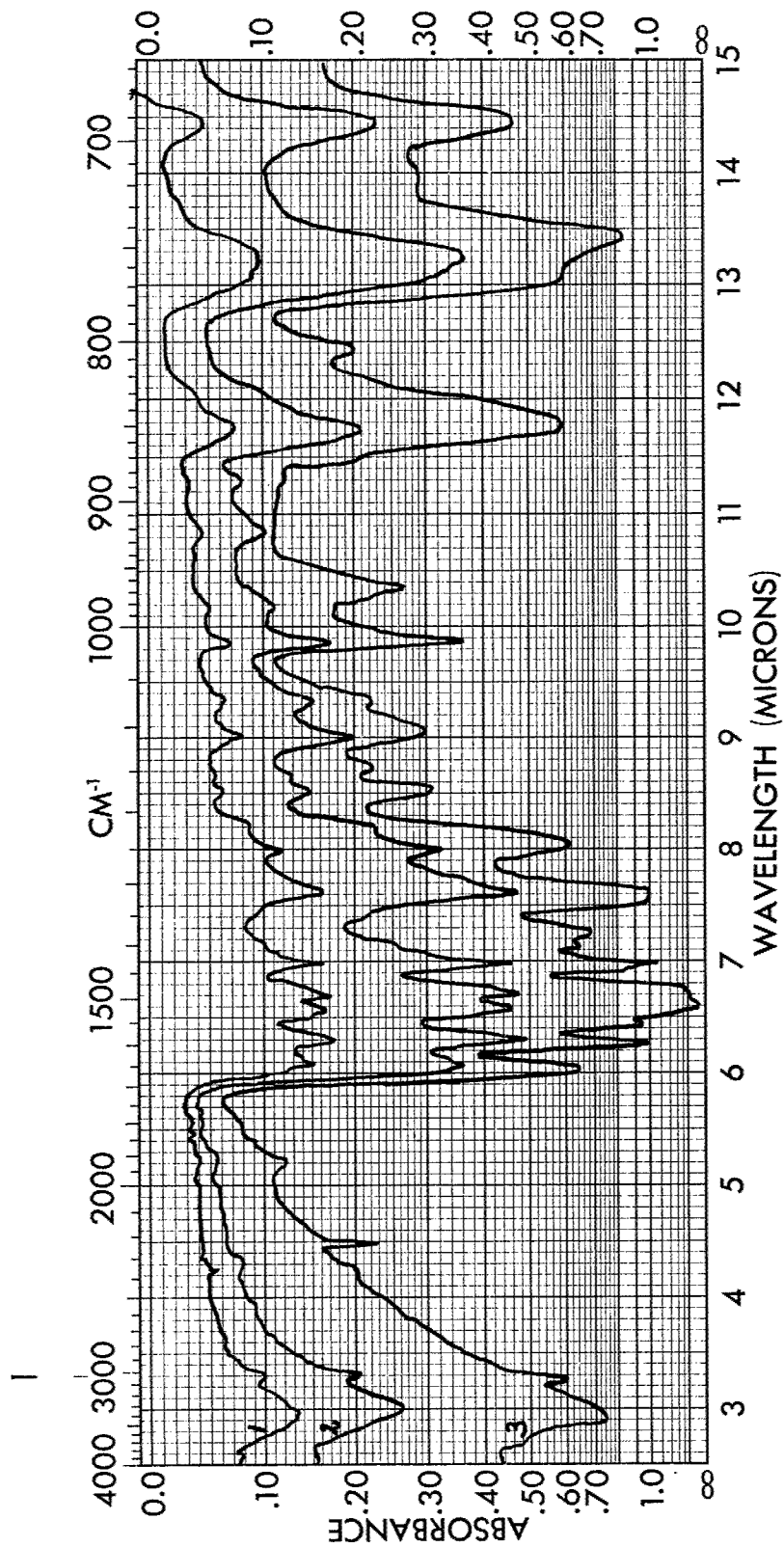


Figure 2. Infrared Spectra of 1: Poly(p-phenylene)imino tetraazolate;
2: Residue at 200°C; 3: Residue at 300°C

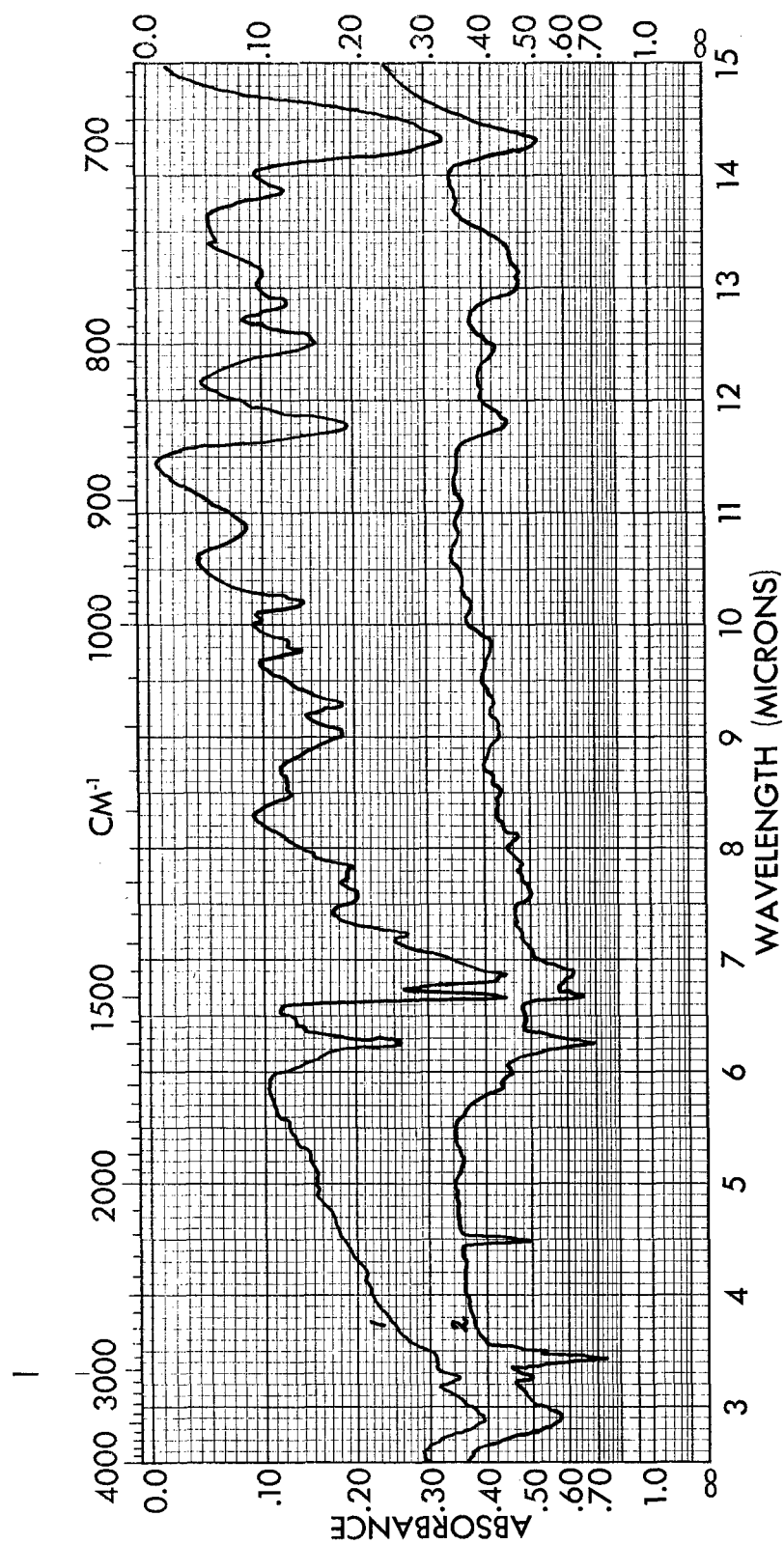


Figure 3. Infrared Spectra of 1: Poly(m-, p-phenylene)-4-phenyl-1,2,4-triazole; 2: Sublimate

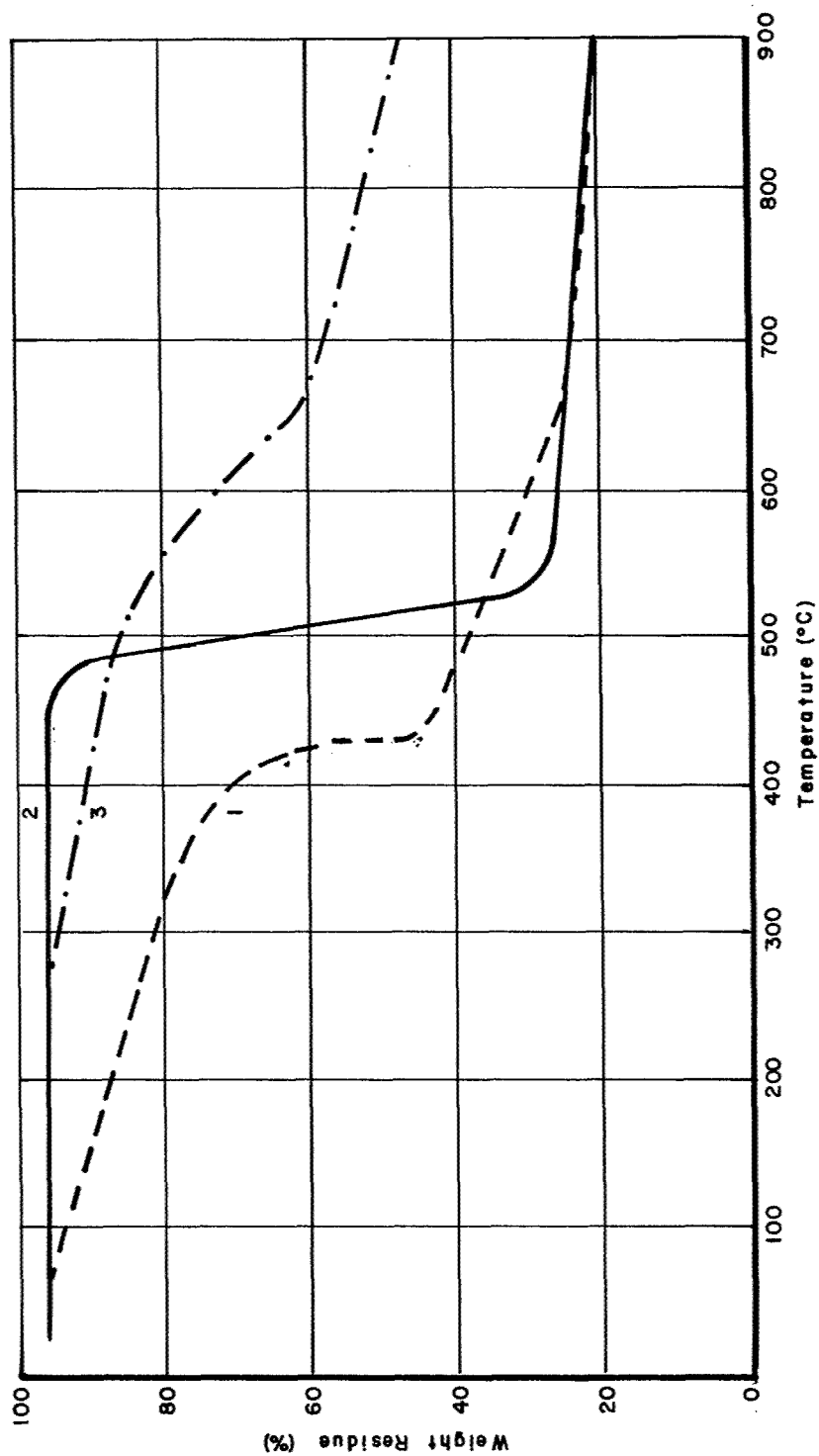


Figure 4. Thermogravimetric Analysis (nitrogen, $\Delta T = 150^\circ\text{C}/\text{hour}$) of 1: Poly(iso/terephthaloyl oxathiahydrazide); 2: Poly(m-phenylene)-1,3,4-thiadiazole; 3: Poly(p-phenylene)-dithiazole

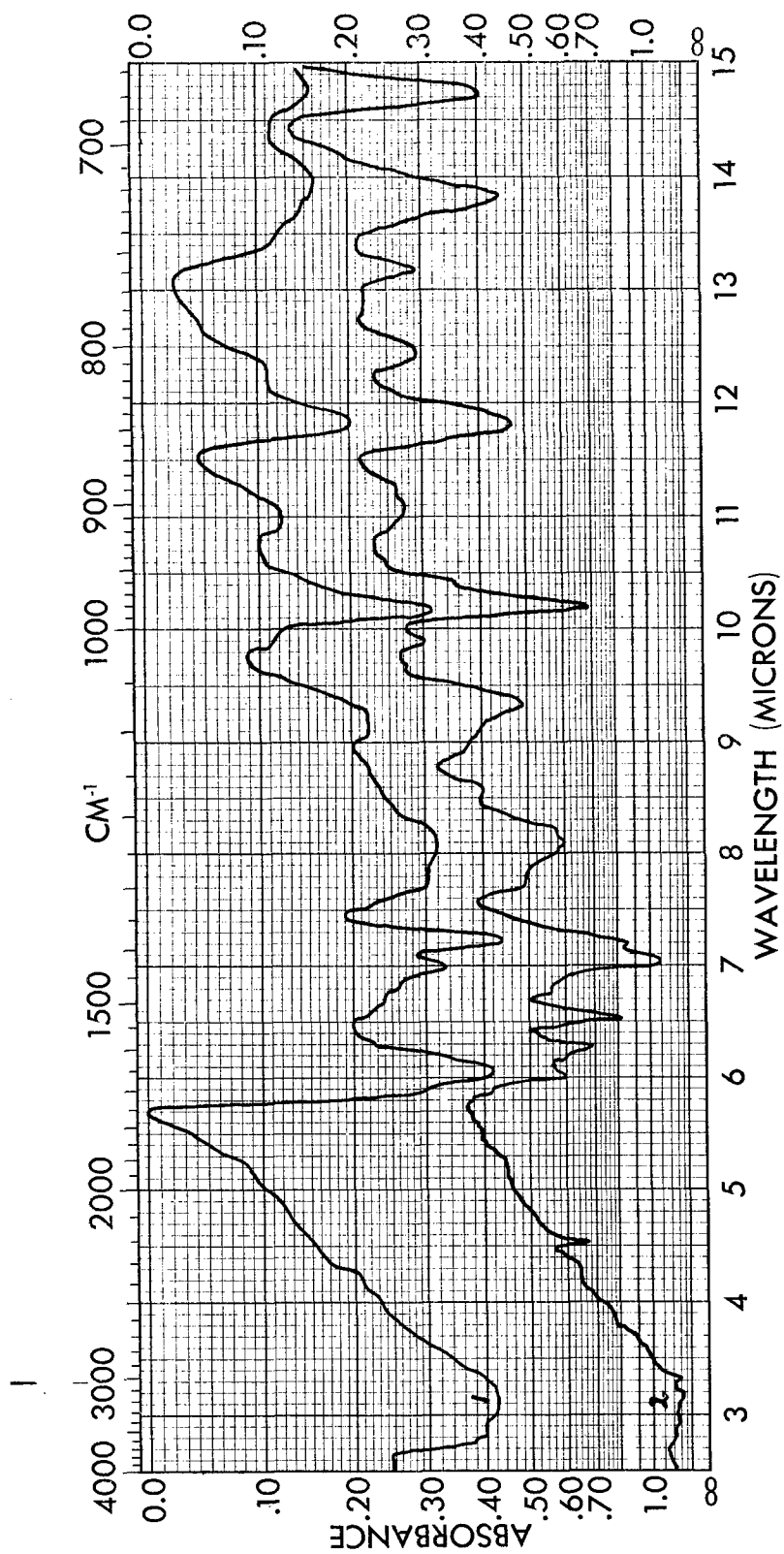


Figure 5. Infrared Spectra of 1: Poly(iso/terephthaloyl oxathiadiazide)
2: Residue at 280°C

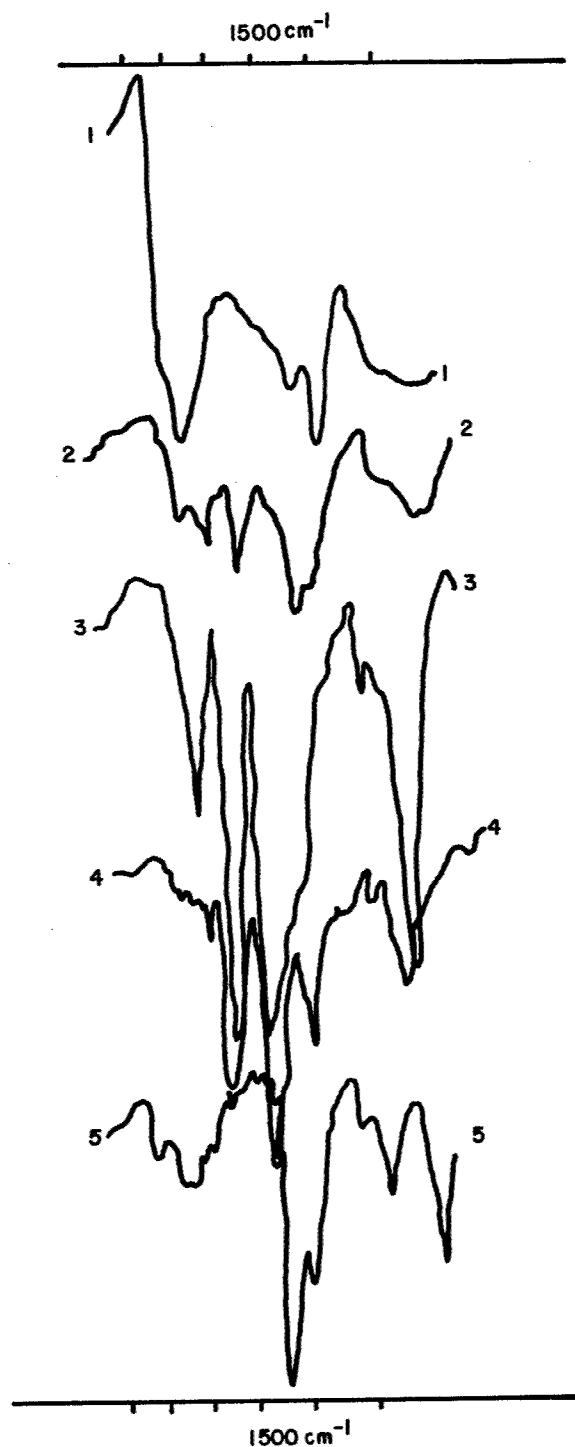


Figure 6. Infrared Spectra of 1: Poly(iso/terephthaloyl oxathiahydrazide); 2: Its Residue at 280°C; 3: Poly-1,3-phenylene-2,5(1,3,4-oxadiazole); 4: Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole); 5: Poly(m-phenylene)-1,3,4-thiadiazole.

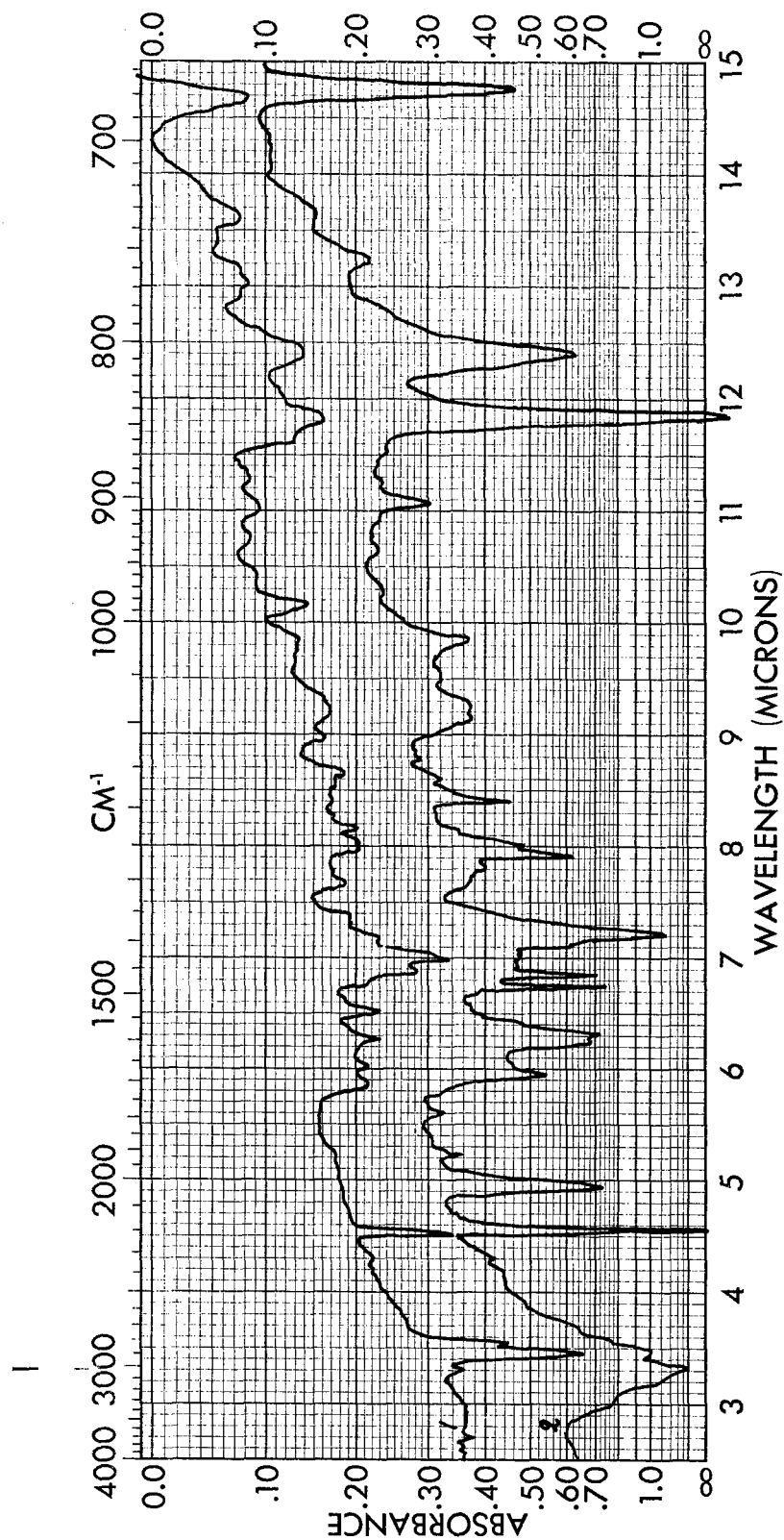


Figure 7. Infrared Spectra of Sublimates of Poly(iso/terephthaloyl oxathiahydrazide) 1: In the Lower Part; 2: In the Upper Part of the Decomposition Cell

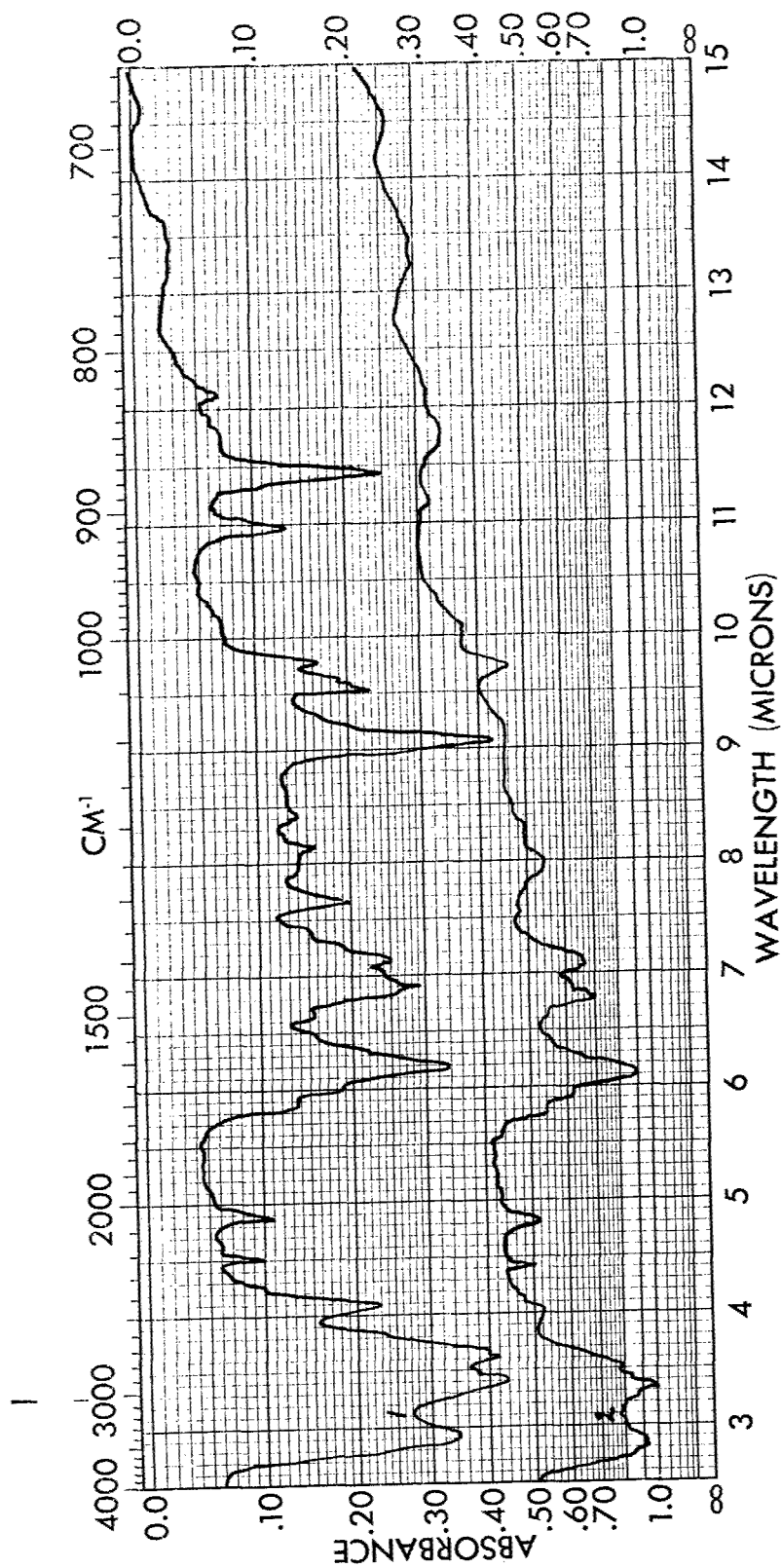


Figure 8. Infrared Spectra of 1: The Water Soluble Fraction of the Sublimate of Poly(iso/terephthaloyl oxathiahydrazide) In the Upper Part of the Decomposition Cell at the End of the 280°C Temperature Step

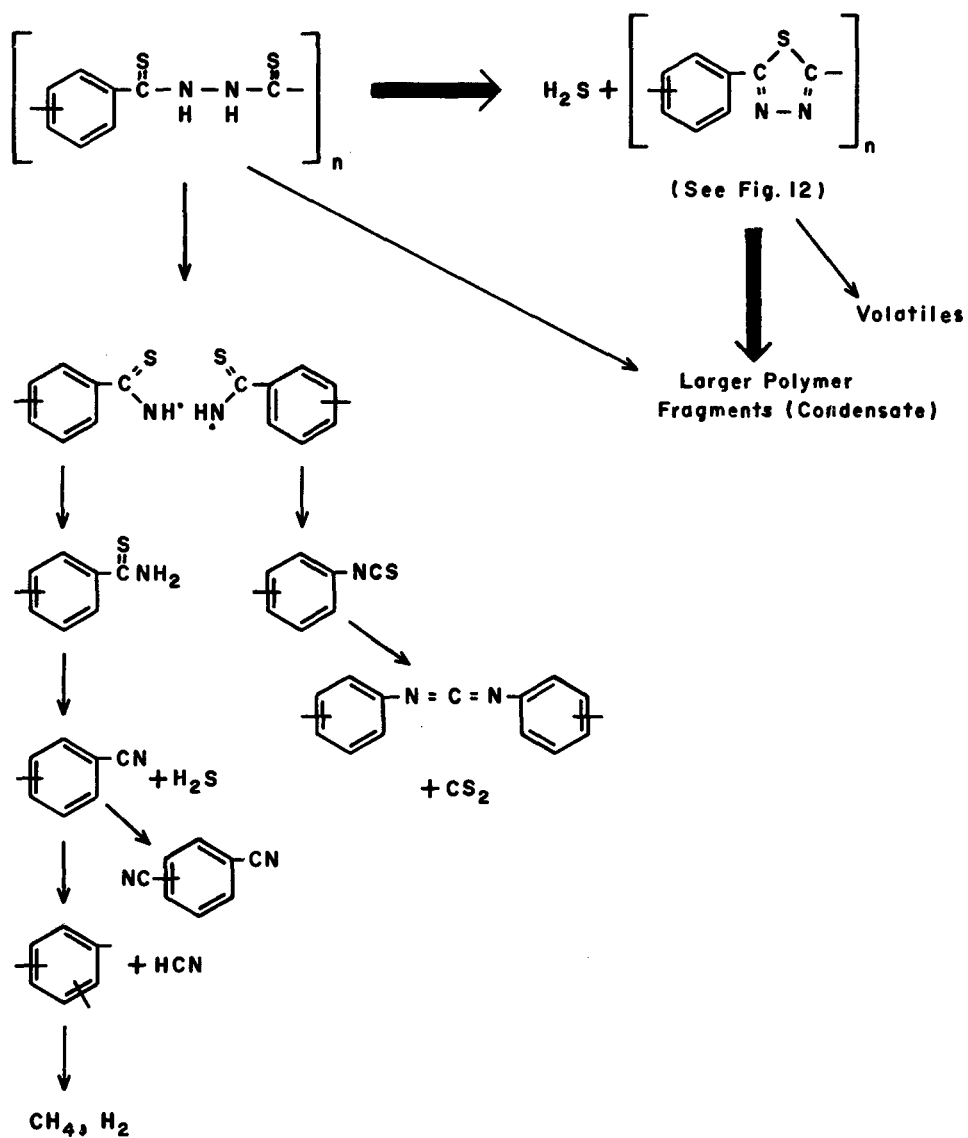


Figure 9. Proposed Breakdown Mechanism of Polythiahydrazides

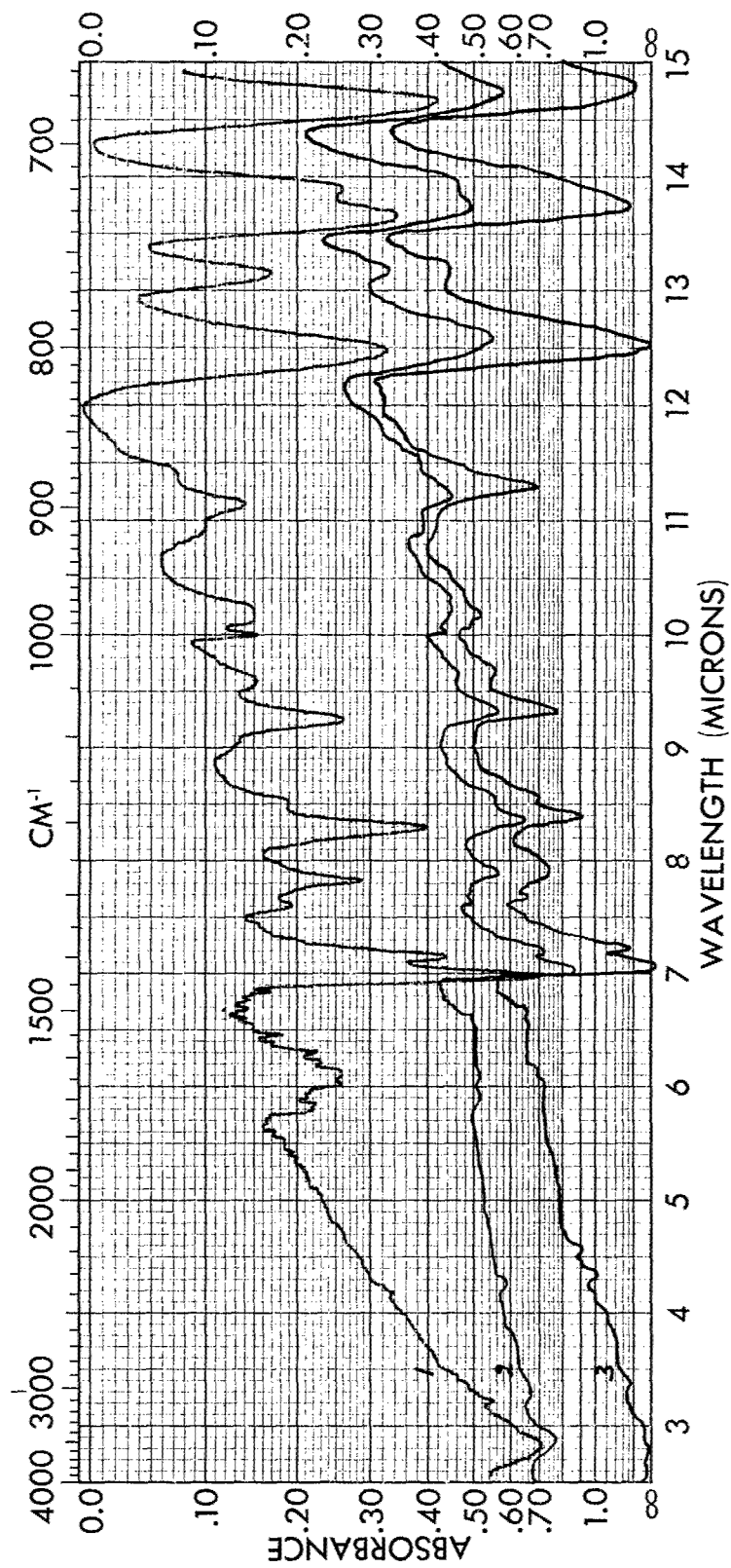


Figure 10. Infrared Spectra of 1: Poly(m-phenylene)-1,3,4-thiadiazole;
2: Residue at 300°C; 3: Residue at 450°C

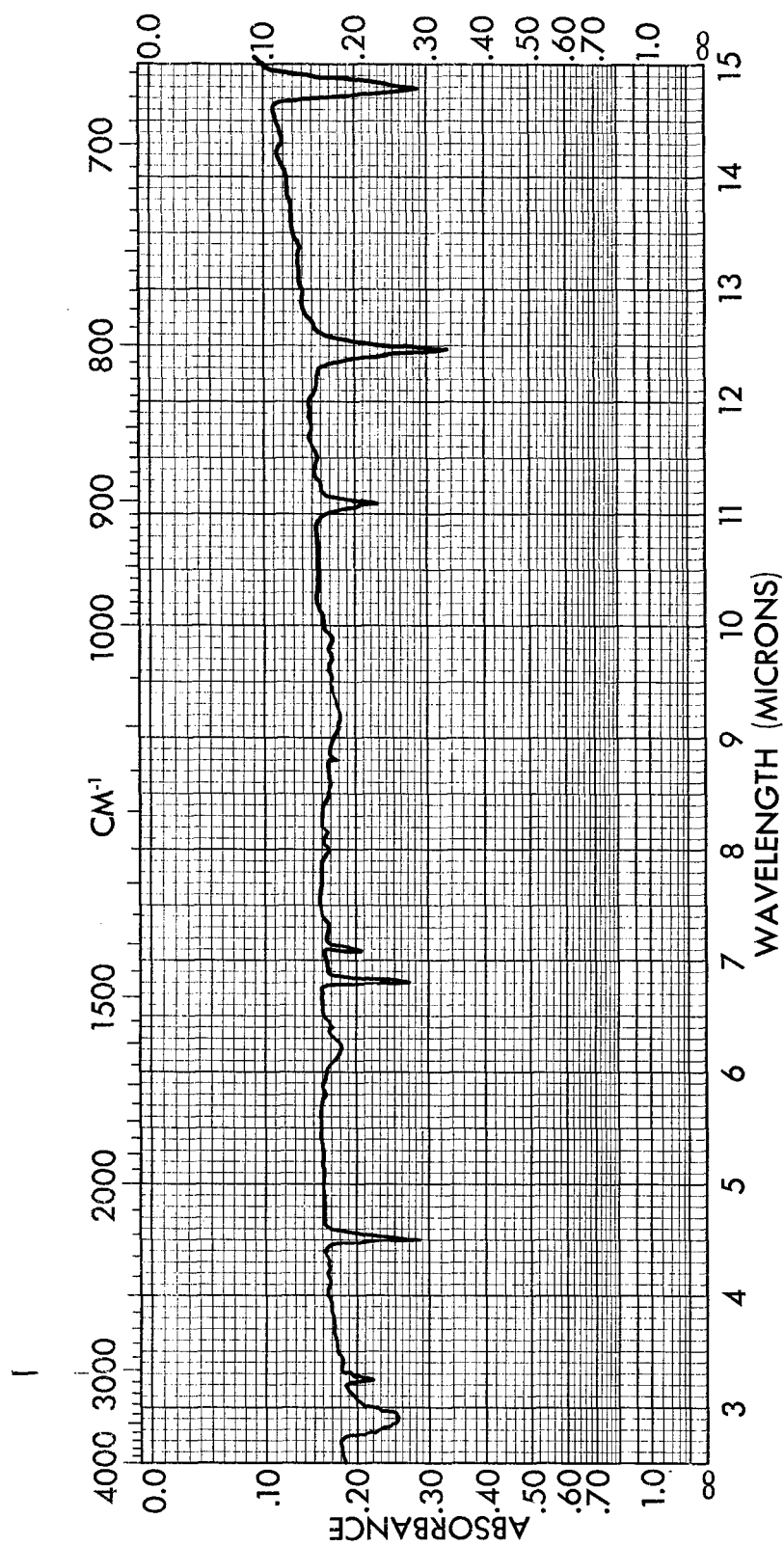


Figure 11. Infrared Spectrum of the Sublimate of Poly(m-phenylene)-1,3,4-thiadiazole

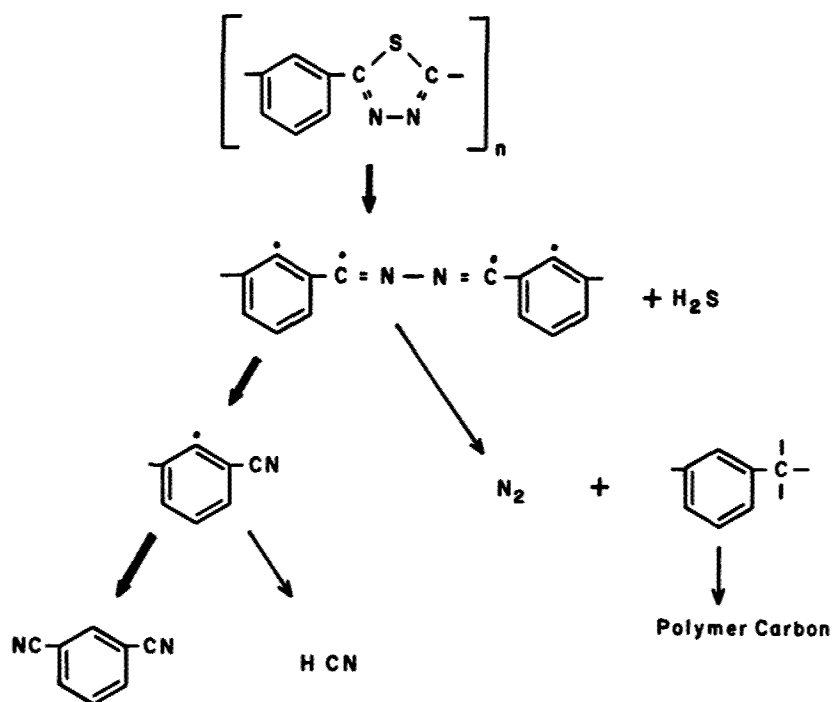


Figure 12. Proposed Breakdown Mechanism of Polythiadiazoles

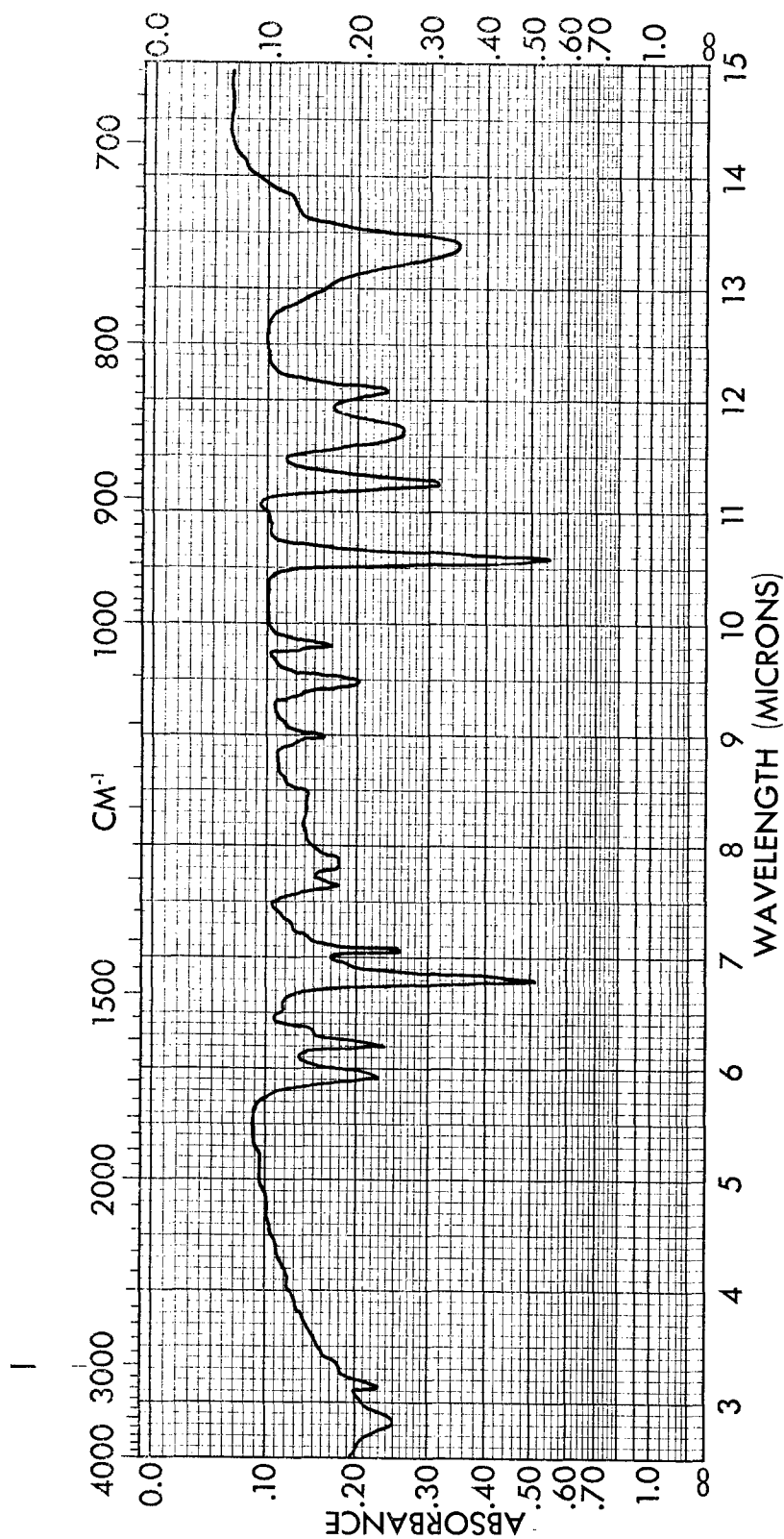


Figure 13. Infrared Spectrum of Poly(p-phenylene)-dithiazole

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UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE STUDIES OF THE BREAKDOWN MECHANISM OF POLYMERS VIII. The Thermal Decomposition of a Poly Tetraazolate, Triazole, Oxathiahydrazide, Thiadiazole, and Thiazole			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
5. AUTHOR(S) (First name, middle initial, last name) Gerhard F. L. Ehlers Kurt R. Fisch, Wilbert R. Powell			
6. REPORT DATE March 1973		7a. TOTAL NO. OF PAGES 38	7b. NO. OF REFS 6
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-72-262	
b. PROJECT NO. 7340			
c. Task No. 734004		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio	
13. ABSTRACT <p>A poly(phenylene)imino tetraazolate, a poly N-phenyl-triazole, a poly-oxathiahydrazide, a polythiadiazole, and a polydithiazole were subjected to decomposition in vacuum at temperatures up to 620°C, and the decomposition mechanisms postulated on the basis of the mass spectroscopic data of the volatiles and the mass spectral, infrared, and elemental analysis of condensibles and residues.</p> <p>A summary of the proposed mechanisms is given in Section IV.</p>			

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
1. Pyrolysis						
2. Degradation						
3. Decomposition						
4. Thermal stability						
5. Mechanism						
6. Mass spectroscopy						
7. Polymer						
8. Poly tetraazolate						
9. Poly triazole						
10. Poly oxathiahydrazide						
11. Poly thiadiazole						
12. Poly thiazole						

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